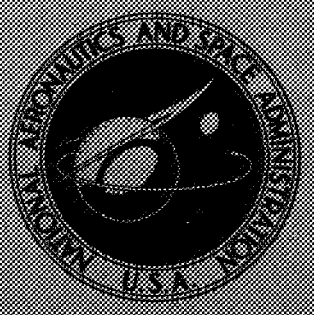
NASA TECHNICAL TRANSLATION




NASA TT F-185

NASA TT F-185

# THE DEPOSITION OF VACUUM COATINGS BY MEANS OF ELECTRON BOMBARDMENT

*by V. K. Pereverzev*

*From Trudy Instituta Metallurgii imeni A. A. Baykova, Akademiya Nauk SSSR,*
No. 11, 1962

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1963

TECHNICAL TRANSLATION F-185

# THE DEPOSITION OF VACUUM COATINGS BY MEANS OF ELECTRON BOMBARDMENT*

By V. K. Pereverzev

From Trudy Instituta Metallurgii imeni A. A. Baykova,
Akademiya Nauk SSSR
No. 11, pp. 209-220, 1962

*Translation of "Protsess naneseniya pokrytiy v vakuume s primeneniyem elektronnoy bombardirovki"

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

# THE DEPOSITION OF VACUUM COATINGS BY MEANS OF ELECTRON BOMBARDMENT

V. K. Pereverzev

At the present time more and more attention is being paid to the many processes of vacuum metallurgy, including methods of depositing vacuum coatings.

Since 1946 the method of depositing coatings by evaporating and condensing the starting materials in a vacuum has been widely adopted by various branches of industry in many countries [1]. The problem of obtaining vacuum coatings is of particular interest in some of the most rapidly developing areas of technology. New prospects are offered by the possibility of using electron bombardment to obtain comparatively thick vacuum coatings of heat-resistant alloys and compounds and their diffusion into the base material.

The method of vacuum deposition is now being used extensively both in the Soviet Union and abroad to produce components for miniature, lightweight electronic equipment with negligibly small power requirements (resistors, capacitors, triggers for computers and binary scalers, thin-film diodes, transistors, etc. [2]. Radically new designs of thin-film radio electronic equipment, suitable for metallurgical purposes, have also been developed in our laboratory.

A large number of experiments has been carried out to obtain and utilize semiconductors and metals in the form of thin coatings with given properties. Many problems, however, still remain to be solved.

The properties of thin films of metals and conductors depend mainly on their composition and structure [3], which are functions of the general crystallochemical laws of the individual condensed element, compound or alloy, determined in their turn by its constitution and characteristics, the conditions of deposition, and

possible after-treatment.

Hence, the study of the deposition of coatings with specific properties is an urgent problem of modern metallurgy.

The investigation of the process of deposition of coatings in a high vacuum using electron bombardment is part of this problem.

## STATEMENT OF THE PROBLEM

Under present conditions any solution must depend on the development and investigation of new processes of depositing coatings by the evaporation and condensation of the starting materials in a high vacuum and the corresponding technology. The reasons for this are as follows.

First, the decisive factor determining the electrical properties of thin films is the state of the surface of the film itself and of the base on which it is deposited [4]. In order to obtain a surface layer with conduction of a given sign, it is necessary to be able to obtain a sufficiently pure surface; this, however, is not easy because of the frequency of defects, impurity centers, and surface states with different properties. The investigations of N. D. Morgulis and others have shown that to some extent it is possible to obtain a sufficiently pure surface in a superhigh vacuum of the order of $10^{-9}$-$10^{-10}$ mm Hg.

The quality of the coating also depends on the purity of the substance evaporated and on the degree of contamination of the coating during evaporation by the residual gases and volatile matter derived from the operation of the evaporator. If the vacuum is not sufficiently high, atoms of the metal being evaporated are scattered by the molecules of residual gas; this retards the growth of the film and distorts the distribution of the condensate. A more serious effect of the residual gas on the properties of the film is the interaction between gas molecules and the substance evaporated at the surface of the condensate. The presence among the residual gases of heavy organic compounds, entering the chamber from the oil pumps and easily adsorbed on pure surfaces, is particularly unfavorable. A number of authors [5, 6] have noted that the properties of the film can be signally

improved by carrying out the evaporation at high speed and in as high a vacuum as possible.

In the present state of vacuum technology it is possible to deposit coatings in a vacuum of the order of $10^{-8}$-$10^{-9}$ mm Hg.

Secondly, we still do not possess sufficiently refined methods of controlling certain of the conditions of vacuum deposition or the quality of the coatings during deposition. The same applies to the corresponding apparatus. Estimates of these conditions and the quality of the coating are often based on the results of checking the finished film and are usually made after the process of deposition has been completed. A great deal of time, of the order of several hours, elapses between the check on the quality of the coating and the regulation of the conditions of deposition from the results of this check.

The achievements of measuring and vacuum technology, automatics, telemechanics, and electronics are making it possible to eliminate this shortcoming.

Thirdly, the present transition to molecular or microcircuits in the manufacturing of radio electronic equipment is mainly based on "molecular metallurgy." Molecular beam control has made it possible to use the method of vacuum evaporation and condensation to obtain not only individual electronic components but whole units. There are prospects of obtaining new alloys and compounds, the need for which is especially great in semiconductor electronics.

As long ago as 1929, Academician S. A. Vekshinskiy showed that new alloys can be obtained in film form by the simultaneous vacuum evaporation or sublimation of several metals from different evaporators [7]. But this method only gives films of variable composition and it is difficult to reproduce consistently only point areas of uniform composition.

Since the use of alloys and compounds is continuously increasing, it is necessary to seek new methods free of these disadvantages. One of the most promising techniques of vacuum evaporation of metal alloys to obtain films with uniformity of composition over their entire surface is the method of phase-dynamic evaporation developed under the direction of P. K. Oshchepkov.

The idea is to have a molecular flux in which a definite ratio of the molecules forming a given alloy is preserved for a known time. It is also necessary that the molecules in the flux be statistically mixed.

The study of such methods and their use in depositing coatings of complex composition with given electrical properties is another very important and still unsolved problem.

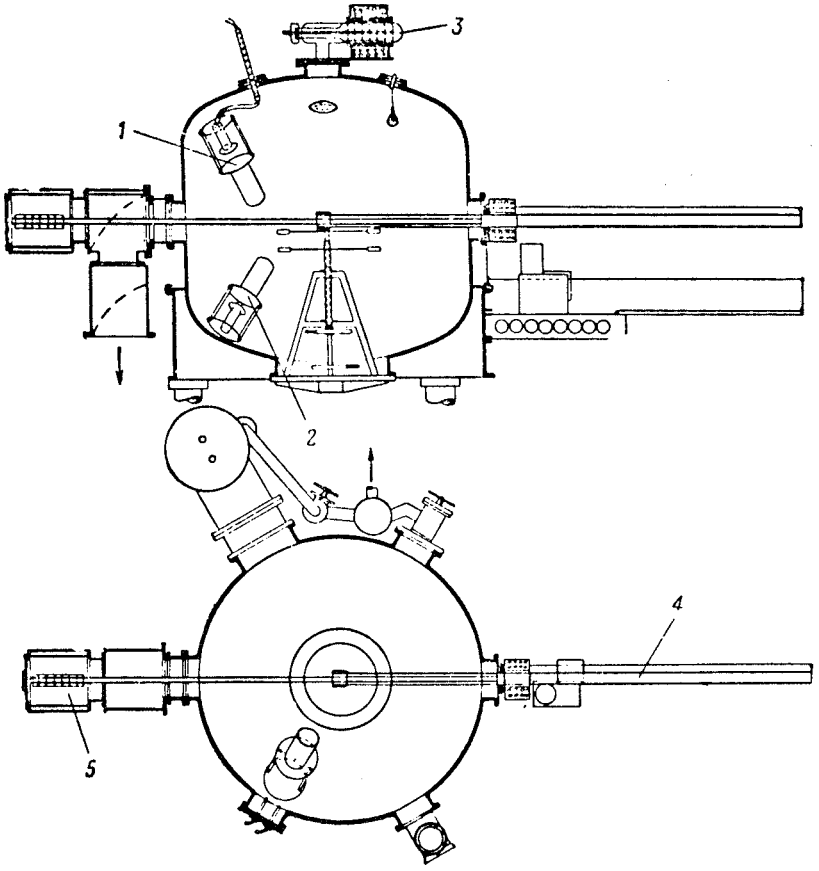
Thus, under present conditions, from both the theoretical and the practical points of view, the most interesting approach to the solution of the problem of obtaining coatings of complex composition with given properties is the development and study of processes of depositing coatings of exceptionally pure materials and coatings of complex composition in a high or superhigh vacuum with control of quality and conditions during deposition.

## DEVELOPMENT AND STUDY OF A PROCESS OF DEPOSITING COATINGS IN A HIGH VACUUM USING ELECTRON BOMBARDMENT

On the basis of the results of a preliminary study of the conditions, under the influence of which the composition and structure of the starting materials change when homogeneous polycrystalline films are obtained by evaporation and condensation in a vacuum, we built and tested a special vacuum sphere (Figs. 1-3). Beginning in 1959 we used it to carry out an experimental study of the application of electron bombardment to the vacuum deposition of coatings of various materials, in particular certain substances, such as tungsten and tantalum, with high melting points, semiconductor compounds, and even dielectrics (glass).

The volume of the vacuum sphere, equal to 1 cubic meter (diameter 1.2 m), was determined by the arrangement of the evaporation source, the working table, the auxiliary devices, and the measuring and control apparatus. The walls of the vacuum sphere were made of 1Kh18N9T stainless, nonmagnetic steel 12 mm thick. In order to accelerate the degassing of the walls, the vacuum sphere was equipped with heating and cooling systems based on "TEN"-type electric heaters and radiators. The bottom hatch, on which the working table and auxiliary devices, and an electron gun are mounted, has an elevating mechanism. Four of the six lateral hatches are designed for the VA-2-2-type main vacuum assembly, an antechamber, the vacuum lock mechanism, and a

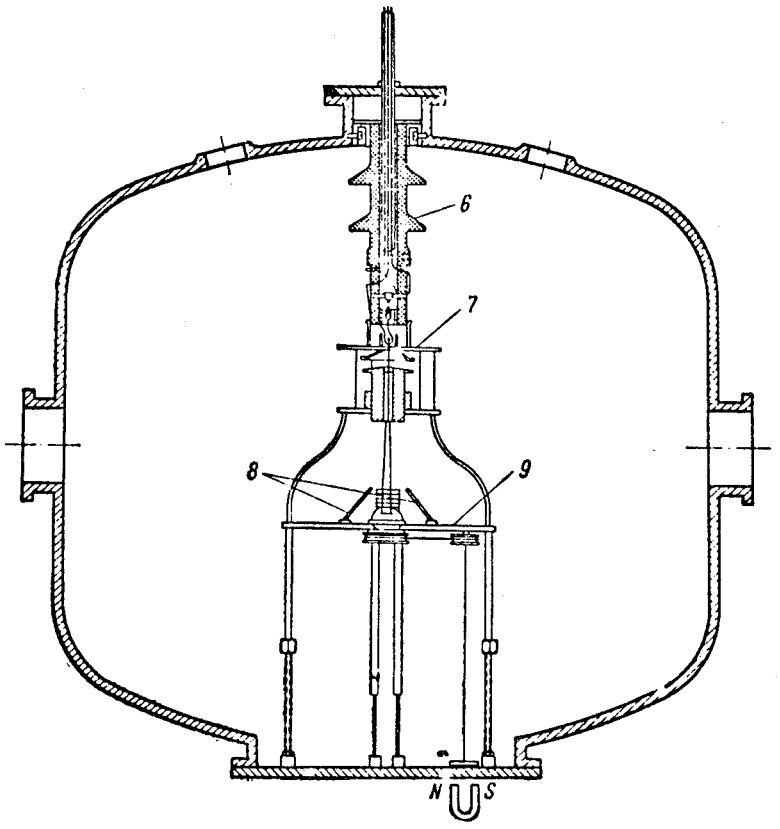
Fig. 1. General view of vacuum sphere.




a

Fig. 2. Two different ways (a and b) of arranging electron guns in the vacuum sphere.

1 - electron gun for heating starting substance, 2 - the same for pre-heating the base, 3 - ion-sorption pump, 4 - vacuum lock mechanism, 5 - antechamber




b

Fig. 2 6 - high-voltage input,

7 - electron gun,

8 - specimen,

9 - table.

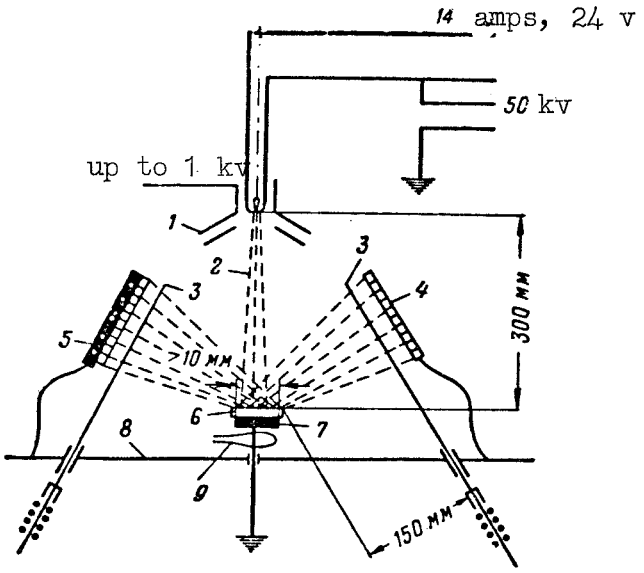



Fig. 3. Diagram to illustrate deposition of PbO films in a high vacuum using electron bombardment:

1 - electron gun, 2 - direction of electron beam, 3 - baffle, 4 - specimen base, 5 - preheater, 6 - starting product (PbO plate), 7 - anticathode, 8 - working table, 9 - ring cathode of lower electron gun.

periscope, while the two remaining positions are intended for an electron diffraction apparatus and an electron mirror now being developed. The five upper hatches are designed to receive the vacuum-tight, high-voltage electric input, the lighting leads, the measuring instruments and pickups, the glass inspection panel, and a dosing device. The bottom hatch also carries 14 leads for supplying the auxiliary ring-cathode electron gun, the heaters, and other devices.

By means of VA-2-2 and VA-05-1 vacuum units, the vacuum sphere can now be reliably evacuated to give a vacuum of the order of $10^{-6}$-$10^{-7}$ mm Hg.

An ion-sorption device capable of giving a vacuum of the order of $10^{-8}$-$10^{-9}$ mm Hg is being installed. An improved type of cold-cathode ion-sorption pump [8] is being studied. This pump does not require special supervision and is designed to maintain a superhigh vacuum during the night and during intervals between shifts. It should be noted that ion-sorption devices, including pumps, do not employ a working fluid. Therefore, molecules of organic compounds cannot appear in the residual gases when such pumps are used to create a vacuum.

Electron bombardment was employed because, as compared with other sources of heat, it has the following important advantages:

1. Even the most high-melting conductors can be fused and evaporated under vacuum conditions.

2. The electron beam does not introduce impurities into the starting materials; in working with particularly pure materials the electron beam and the molecular flux can be directed at different angles.

3. The power of the electron beam is easily regulated, so that the rate of evaporation of the coating material can be varied.

4. By focusing it is relatively easy to vary the dimensions of the focal spot of the electron beam, so that different areas of the starting material can be heated with the same beam.

5. By displacing the focal spot of the electron beam and varying its size it is possible to carry out a number of

technical operations -- heating, welding, fusing, evaporating, and the fine cleaning of the surfaces on which the coating is deposited.

Besides having superior technical properties, electrons are abundantly available and easily obtained. The electron beam is accelerated, focused and deflected in the time taken for the electrons to leave the cathode of the electron gun and disappear in the anode (of the order of $10^{-8}$ seconds).

In Fig. 4 the electron gun that created the powerful rectilinear electron flux used in our experiments is shown in schematic form. Electron beam 1 is formed as a result of thermionic emission from cathode 2 at a filament current of 16 amps, 24 volts. The electron beam is focused by means of an electrostatic lens close to the cathode, powered by a set of dry cells across a potentiometer. This method of focusing a relatively powerful beam is a new one -- a magnetic lens would normally be used. A rectilinear electron beam of given cross section is obtained by means of parallel electrodes 2' and 3 having the form of equipotential surfaces. The beam is accelerated by forming a potential difference between them (in our case 50 kv).

The electrons penetrate into the substance and interact with the electrons and nuclei of the atoms. As a result of these processes the velocity of the beam changes in magnitude and direction. The absorption curves of a monochromatic electron beam [9] permit us to assume that an electron loses its energy not all at once, but gradually, in small amounts. The energy loss of the electron beam has a maximum at a certain distance from the surface of the anticathode, approximately equal to the range of an electron. Lange and Brasch [10] showed experimentally that a powerful electron beam will evaporate internal layers of metal. The temperature field forms in the course of $10^{-6}$ seconds.

The amount of thermal energy needed to evaporate the starting material is

$$Q = 0.24\ TI \cdot V - Q_1,$$

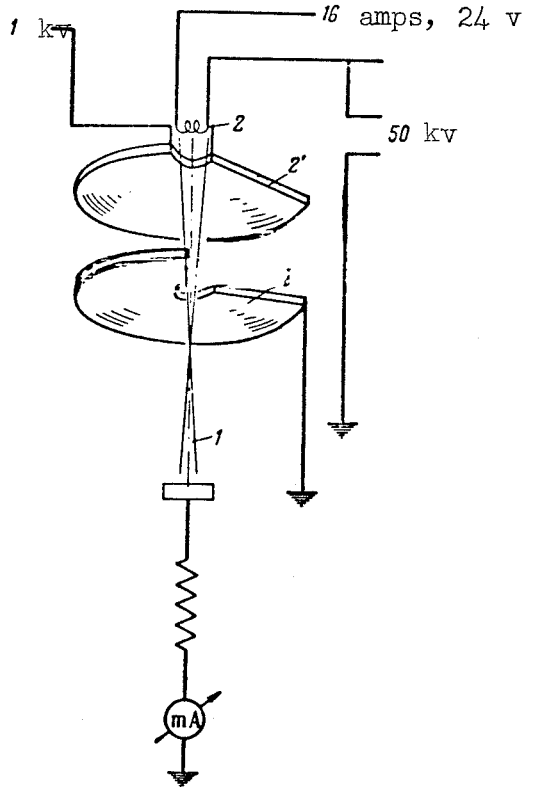



Fig. 4. Schematic drawing of axial electron gun.

where $Q_1$ = total heat loss, cals;

$I$ = current passing through a given section of the anticathode, amps;

$V$ = accelerating potential, volts;

$T$ = time, seconds.

As is known (from T. A. Titova's dissertation), the losses due to x-ray, luminous and thermal radiation during electron bombardment account for an insignificant percentage of the total energy. The intensified evaporation of material affects the nature of the discharge and leads to a reduction in the x-ray dose.

Losses due to the removal of heat through the material of the anticathode can be considerably reduced by mounting the bombarded material on a thin layer of thermal insulator.

Accurate solutions of the space charge equations for the design of electron guns are known only for the case of rectilinear motion of the electrons between parallel plates, concentric cylinders and concentric spheres. In order to obtain such a beam in a specific region, the electrons must enter and leave that region through apertures in parallel electrodes having the form of equipotential surfaces. The form of the equipotentials does not depend on the absolute values of the potentials or the choice of the units determining the distance between electrodes. It can be calculated or else determined with the aid of an electrolytic bath. The latter method has been sufficiently well described by D. R. Pirs [11] and is employed in our laboratory. By this method we found that the electrode mounted close to the cathode should form an angle of $65^\circ$ with the normal to the surface of the cathode.

All in all we investigated six different designs of electron gun, for each of which we studied the following relations:

$$I = f \cdot V, \quad D = \int V, \quad D = \int V_y$$

where I = current passing through a given section of the anticathode, amps,

V = accelerating potential, kv,

$V_y$ = potential applied to the electrostatic lens, v,

D = diameter of focal spot of electron beam, mm.

The data obtained were used to calculate the amount of material evaporated, the evaporating time, and the time required to focus the electron beam.

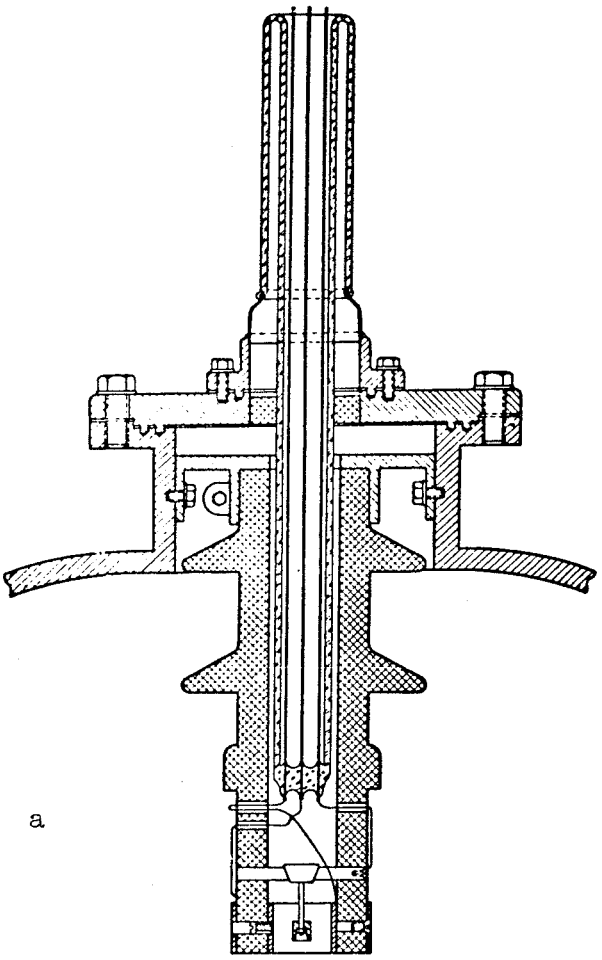
The investigations demonstrated the advisability of using two types of electron gun:

1. with electrostatic focusing of the electron beam, mounted on the working table inside the vacuum sphere (Fig. 5);

2. with a ring cathode, used for heating semiconductors with a high resistance (Fig. 3).

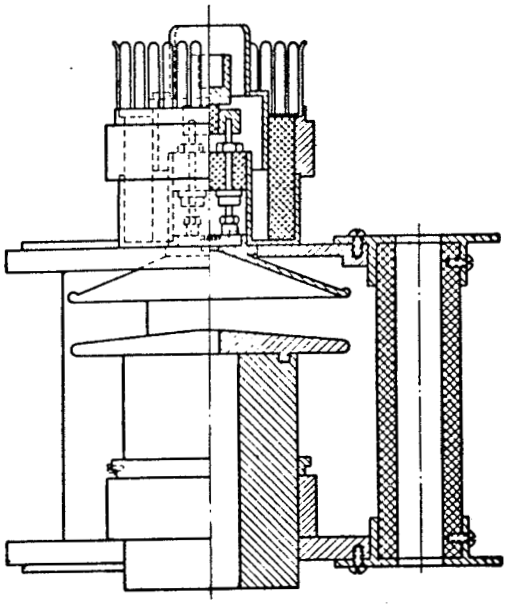
A series of devices and attachments was developed to make it possible to carry out the entire deposition process (evaporation or sublimation of the materials, transfer of the molecular flux, condensation) under controlled conditions. These included devices for moving the materials and specimens inside the vacuum sphere, for providing a visual representation of the electron beam, for holding back a contaminated molecular flux (the most original was an eight-lobed baffle), for heating the specimens, etc. We also developed a radically new lock mechanism for introducing specimens and materials into the vacuum chamber without disturbing the vacuum. A preliminary determination of the conditions of deposition was normally made in a small vacuum apparatus.

An examination of the behavior of a substance in a vacuum when the temperature is raised demonstrates the advisability of separately studying the process of deposition when the molecular flux is propagated against (Fig. 6, A) and in the direction of (Fig. 6, B) the path of the electron beam.



a

Fig. 5. Electron gun (b)
with high-voltage input (a).



b

Fig. 5.

From the constitution diagram it follows that if a low pressure (lower than that at the triple point) is created over a single-component substance, then the application of heat will lead to sublimation. We have this case when the molecular flux is propagated against the electron beam. It is known that when a pressure of the order of $10^{-6}$ mm Hg is developed near the evaporating surface, evaporation proceeds virtually in the form of a molecular flux. The laws of geometric optics then become applicable and hence it is expedient to study the possibilities of deflecting and screening molecular fluxes. Providing the conditions for

sublimation (i.e., high or superhigh vacuum and high temperatures at the heating surface) is useful from the point of view of excluding the aggressive action of liquid metals and saturated vapors on the surrounding structural materials. The procedure has a disadvantage, however, in that the electron beam to some extent ionizes the maximally dense molecular flux of starting material moving against it. The latter, moving in a space determined by the cross section and length of the electron beam, is, as it were, pinched out and uselessly condenses on the parts of the gun.

In this manner it is possible to deposit films between several hundredths of a micron and several microns thick. We have studied the conditions of deposition of films of Al, Cu, Ni, W, Mo, and Ta, of the semiconductors CdS and PbO, and of insulators (glass). The glass was evaporated from the surface of a graphite plate; accordingly, some carbon was included in its composition.

The second method of deposition, with the molecular flux propagated in the direction of the electron beam, consists in passing a thin strip of starting material along the normal to the axis of the electron beam with the base mounted very close beneath it (of the order of fractions of a millimeter) (Fig. 6,B). After the material of the strip has been evaporated through over an area equal to the size of the focal spot of the electron beam, part of the molecular flux will be directed along the path of the electron beam and will condense on the surface of the specimen. In the narrow space between the strip of starting material and the surface of the specimen it is possible for a vapor pressure to develop greater than the vapor pressure at the triple point. At the same time, in the vacuum sphere, above the strip, a vacuum of the order of $10^{-6}$-$10^{-7}$ mm Hg is maintained. This is confirmed by the fact that fusion is observed on the underside of the strip. As the strip is moved under the electron beam, a much thicker coating is formed on the surface of the base, much more quickly than under the conditions illustrated in Fig. 6,A. In this case the base, too, is exposed to electron bombardment. The heating of the base and the action of the electron irradiation result in the intensive and deep diffusion of the condensed material. This also explains the greater adhesion between the base and the relatively thick coatings obtained by this method. Experience has shown that this particular technique is suitable for depositing tungsten contacts. Using the same system, on the instructions of the NIKFI AN SSSR [Motion Picture and Photography Scientific

Research Institute, Academy of Sciences USSR], we successfully investigated the deposition of permalloy on ferrite, for a device of the image storage type.

In order to be able to control the quality of the coating and regulate the conditions of deposition, we developed special indicators to measure the electrical resistance of the films during the deposition process. These measurements make it possible to accumulate data for determining the relation between the electrical resistance and the thickness of the layer and the conditions of deposition for different materials. We have partly developed an electron diffraction apparatus for the vacuum sphere. With the aid of a "Unikon" electron converter (designed in our laboratory) an image of electron diffraction pictures of the film, periodically obtained during the process of deposition in the vacuum sphere, can be reproduced on a television screen and, if necessary, photographed. Thus, it is possible to obtain information on the fine structure of the films at various times, not in the equilibrium state alone. A model of an electron mirror was developed for the visual observation of the potential distribution at the surface of a semiconductor coating, to obtain an image of the pn junction, and the pattern of secondary electron emission from the pn junction.

We also measured the Hall effect on the films. The further development of methods of measuring this effect during the deposition process, and of determining the conductivity of the films, is a matter of considerable interest. From the Hall effect and the conductivity it is possible to determine the type of conduction, and the density and mobility of the carriers. Hence, it is possible to obtain all the principal electrophysical constants, without removing the film from the vacuum sphere, and, where necessary, to find the conditions for obtaining films with desired electrical properties.

In order to control the deposition process, we measured the temperatures at the evaporation point, at the surface of the "crucible" or of the anticathode support for the starting material, at the surface of three specimen bases, mounted at different distances from the evaporating point, and at the inside surface of the wall of the vacuum sphere.

Using electron bombardment, we studied and developed processes of depositing complex films incorporating the compounds CdS, PbO, etc.

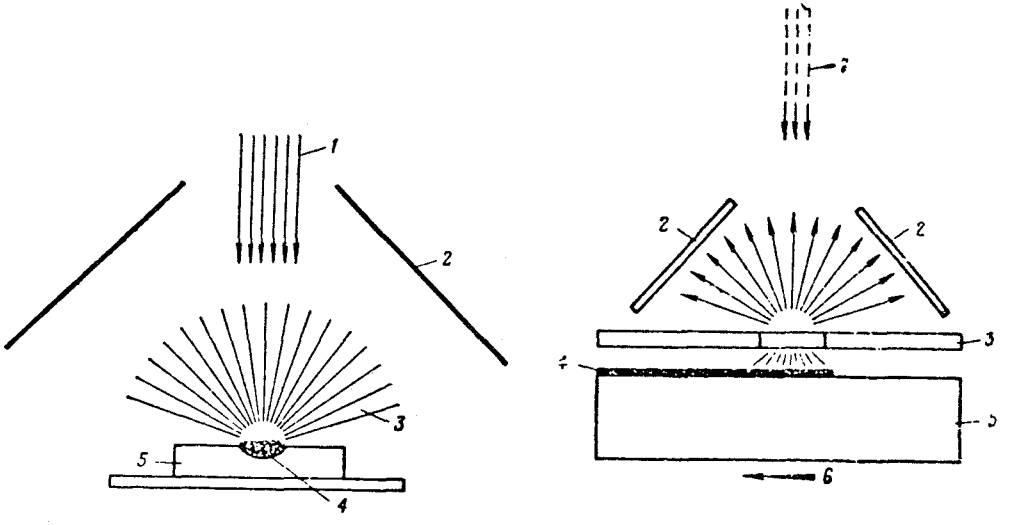



Fig. 6. Deposition of coatings with the molecular flux propagated against (A) and in the direction of the electron beam (B).

A: 1 - direction of electron beam, 2 - base to be coated, 3 - direction of molecular flux, 4 - starting material, 5 - "crucible";
B: 1 - direction of electron beam, 2 - bases for thin coatings, 3 - strip of starting material, 4 - thick coating, 5 - base, 6 - direction of movement.

A comparison of the results of x-ray structural and electron diffraction analysis of the starting substances and the films showed that under definite conditions the latter may have a composition and structure close to those of the starting material. Our chief problem, however, was to obtain new materials with given properties that could be reliably reproduced.

The study and development of different processes of depositing films made it possible to establish the conditions that give CdS films of the type used in superhigh-frequency detectors.

PbO films gave better results with respect to photoresistance than analogous films obtained by evaporation from a crucible.

The new values of the electrophysical constants of films obtained using electron bombardment may be due to the instantaneous heating of point areas of the starting substance to a temperature considerably in excess of the evaporation point. The rate of diffusion of the components may then be less than the rate of sublimation of the starting substance at the individual points. We should bear in mind that under the action of a powerful electron beam a temperature field is formed in $10^{-6}$ seconds and evaporation of internal layers of metal takes place.

From this point of view, the use of electron bombardment is to be recommended for the evaporation and sublimation of alloys that exfoliate on melting.

The composition, structure, and hence the properties of the films obtained depend on the conditions of the ambient medium. Therefore, even before being removed from the vacuum sphere they are subjected to a series of treatments.

In order to modify their structure, the films may be subjected to heat treatment with the aid of electron bombardment. In order to modify the composition it is possible to use secondary alloying by the method of selective evaporation. The composition and structure can be fixed by depositing a protective coating over the basic film.

By means of electron-beam techniques it is possible to cut out a film of given profile, sinter and solder, and seek new ways of obtaining thin-film semiconductor systems of microminiature components.

## SUMMARY

The Electrophysics Laboratory of the Institute of Metallurgy has built a special vacuum sphere in which it is possible to carry out the process of depositing thin films by the method of evaporating and condensing very high-melting substances in a high or superhigh vacuum using electron bombardment, together with control of the quality of the coating and the conditions of deposition.

Several different forms of the deposition process have been investigated in relation to a series of metals.

The laboratory has developed methods of studying the process of deposition of films of complex composition.

## BIBLIOGRAPHY

1. Mur, D., Perspektivy vakuumnoy metallurgii (The Prospects of Vacuum Metallurgy), in "Vakuumnaya metallurgiya" (Vacuum Metallurgy), a collection of articles. Foreign Literature Publishing House, 1959.
2. Klass. Puti razvitiya aviatsionnoy elektroniki (The Future of Aviation Electronics), translation from the English. In the collection "Radioelektronnaya promyshlennost'" (The Radio Electronics Industry), 1959, No. 9.
3. Konozenko, I.D., Fizika tonkikh sloyev (The Physics of Thin Films), UFN (Progress in the Physical Sciences), Vol. 52, No. 4, 1954.
4. Introductory article in the collection: "Fizika poverkhnosti poluprovodnikov" (Semiconductor Surface Physics), Foreign Literature Publishing House, 1959.
5. Vinogradov, M. I., Tekhnika ispareniya metallov (The Technology of Evaporating Metals), PTE (Experimental Equipment and Techniques), No. 8, 1960.
6. Espe, V., Napyleniye tonkikh plenok v vysokom vakuume (Vacuum Deposition of Thin Films), in the collection "Radioelektronnaya promyshlennost'", No. 20, 1959.

7. Vekshinskiy, S.A., Novyy metod metallograficheskogo issledovaniya splavov (A New Method for the Metallographic Investigations of Alloys), OGIZ (State United Publishing House), Tekhizdat, 1944.
8. Reykhrudel', E. M. and Smirnitskaya, G., Ionnyy nasos s kholodnymi elektrodami (An Ion Pump with Cold Electrodes), Radiotekhnika i elektronika (Radio Engineering and Electronics), No. 2, 1956.
9. Scholand, B. F. Proc. Roy. Soc. (L), 1928, Vol. 104, 235; 1925, Vol. 108, 187.
10. Lange, F. and Brasch, R. Strahlentherapie, (Radiation Therapy) 1931, Vol. 50, 119.
11. Pirs, D. R., Teoriya i raschet elektronnykh puchkov (Theory and Design of Electron Beams), "Sovetskoye radio" Press, 1956.

FARADAY TRANSLATIONS
15 PARK ROW
NEW YORK 38, N. Y.

For sale by Office of Technical Services, Department of Commerce,
Washington, D. C. Price $0.75